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USSR TRENDS IN WORK ON ORGANIC NITRO COMPOUNDS

[Numbers in parentheses refer to appended sources.]

Introduction

The work on the nitration of hydrocarbons carried out in the USSR by A. I. Titov and described below is of importance, because nitro compounds are used as explosives, components of rocket fuel and propellant mixtures, and as additives improving the combustion characteristics of diesel fuels. A. I. Titov has been identified with the Military Academy imeni K. Ye. Voroshilov, where he is known to have been active during 1947-50. He is also the author of papers which have been published in one case as a joint contribution from the Military Academy imeni K. Ye. Voroshilov and the Scientific Research Institute for Organic Intermediates and Dyestuffs imeni K. Ye. Voroshilov. In another case he was the author of a contribution of the Scientific Research Institute for Organic Intermediates and Dyestuffs imeni K. Ye. Voroshilov, without reference to the military academy. In regard to this, one may assume that research on nitro compounds and investigative work on dyestuff intermediates (i. e., the amines derived from these nitro compounds and the derivatives of these amines) are closely connected and would be carried out at the same institution or institutions, between which close liaison is maintained as far as this work is concerned.

In connection with the fact that A. I. Titov is the author of a paper on nitro compounds published as a contribution from the Military Academy of Chemical Defense imeni K. Ye. Voroshilov (A. I. Titov, N. G. Laptev, Oxidative Nitration of alpha- and beta-Naphthylmercurinitrates, Doklady Akademii Nauk SSSR, Vol 66, 1949, No 6, pp 1001-1003), it is of interest to note that he (together with B. B. Levin) has also published papers on the synthesis of arsines (Sbornik Statey po Obshchey Khimii, Vol II, 1953, pp 1469-1472, 1473-1477, and 1478-1482) and (together with F. A. Maklyayev) has conducted a series of investigations on conjagated reactions of the addition of halogens to olefins in the course of which halogenoethylation in general and the

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chloroethylations of benzenesulfonic acid, p-toluenesulfonic acid, chlorosulfonic acid, sulfuric acid, and phosphoric acid in particular were studied (Zhurnal Obshchey Khimii, Vol 86, No 9, pp 1624-1630, 1631-1635; Vol 86 No 10, pp 1860-1862). Research on these subjects, although it also has other potential applications, may be assumed to have a bearing on work connected with the synthesis of chemical warfare agents.

Research on nitric acid-acetic acid-acetic anhydride systems (see below) is of importance, because mixtures of this composition are used when it is desired to carry out the nitration rapidly and under mild conditions because either the starting material or the final product is very sensitive and unstable. As a rule, the nitration cannot be accomplished by any other means in such cases. A typical example is the nitration of hexamethylenetetramine to cyclotrimethylenetrinitramine (i. e., the preparation of the explosive cyclonite) by this method.

The study of the properties of nitric acid-acetic anhydride mixtures has also a bearing on the production of tetranitromethane (tetan). Tetranitromethane is prepared by reacting acetic anhydride with nitric acid. It is used as an ingredient of explosive mixtures and is also very toxic.

Research on the reduction of nitro compounds to amines (see below) is significant from the standpoint of the use of amines as intermediates for the production of explosives (e. g., tetryl) and as rocket propellants (e.g., aniline in combination with nitric acid).

The general relationships established in research on aromatic nitramines and on the properties of the nitramine group (see below) may find application in work on explosives of the nitramine type.

Nitration of Hydrocarbons

A. I. Titov and one of his collaborators (M. K. Matveyeva) are continuing the extensive investigation on the nitration of saturated hydrocarbons and arylparaffins which has been conducted since the end of World War II under Titov's direction, and which followed a series of investigations on the nitration of aromatic hydrocarbons carried out by Titov and members of the group headed by him.(1) One of the cardinal points of the theory of nitration developed by Titov, on the basis of his investigations, is the assumption that a free alkyl radical or a radical derived from a hydrocarbon of some other type is formed as a result of a collision between the molecule of the hydrocarbon and monomeric nitrogen dioxide. According to Titov, the radicals thus formed then combine with nitrogen dioxide. Titov assumes that nitrogen dioxide rather than nitric acid is the active nitrating agent, and that nitric acid is effective in nitrations merely because it furnishes nitrogen dioxide which acts as the nitrating agent, and because it regenerates nitrogen dioxide from the lower oxides. He states that, according to his theory, nitric acid as such does not exert any nitrating or oxidizing effect. This theory is reiterated in an investigation on the mechanism of the oxidation and nitration of cyclohexane recently begun by Titov and Matveyeva. These investigators state that their theory has been fully confirmed by the experimental results obtained hitherto in work on cyclohexane. They found that the interaction of cyclohexane with nitrogen dioxide proceeds at a relatively high velocity and yields the same products as nitration with nitric acid by the method of S. S. Nametkin and M. I. Konovalov. They also found that addition of titanium tetrachloride, aluminum chloride, or sulfuric acid does not affect the course of the reaction, and cite this result in support of the assumption that the reaction is of the radical rather than ionic type. They finally established in experiments carried out at 320°-340° that the yield of reaction products resulting from the interaction of cyclohexane with nitrogen dioxide is 10 times higher than the yield obtained in the interaction of cyclohexane with nitric acid.(2)

In another phase of the investigation on the nitration of cyclohexane, Titov and Matveyeva found that the general theory of nitration which has been developed by Titov is supported by results obtained both on cyclohexane and n-pentane. They determined that cyclohexyl nitrate, cyclohexyl nitrite, cyclohexanol, and cyclohexyl adipates are formed when cyclohexane is nitrated and that amyl nitrites are formed under similar conditions from n-pentane. They furthermore found that the relative yield of oxidation products rises when the concentration of nitrogen dioxide is increased, and they regard this result as a confirmation of Titov's theory of nitration. In the published paper which deals with this phase of the investigation, Titov and Matveyeva discuss in some detail the mechanism of the formation of adipic acid from cyclohexane that has been subjected to the action of nitric acid and/or nitrogen dioxide.(3)

In a recent paper of a series dealing with the general mechanism of the nitration of saturated hydrocarbons Titov and Matveyeva report experimental results which indicate that the specific nitrating action of nitric acid under pressure, which is assumed by Konovalov, is due to the fact that the equilibrium

$$2\ HNO_3 + NO \rightleftharpoons 3\ NO_2 + H_2O$$

shifts to the right, an effect which is particularly important in the latter stage of the reaction, when the concentration of NO is high and that of nitric acid low. They also describe experiments on the effect of diffusion of NO_2 into the hydrocarbon phase. They found that the reaction yields and the type of the reaction products obtained are very strongly affected by changes in the rate of diffusion brought about by modifying the temperature, applying agitation, and using reaction vessels of different cross sections. According to the data reported in this paper, lagging of the diffusion process behind the reaction process increases the proportion of products of the transformation of nitroso compounds, expedites the formation of mononitro compounds, and leads to a reduction of the yield of oxidation products.(4)

In a paper dealing with the catalytic nitration of aromatic hydrocarbons in the presence of mercury salts, Titov describes an investigation of the mechanism of nitration of toluene and presents data showing that the yield of nitrotoluenes is higher when the concentration of nitrogen dioxide is greater.(5)

Research on Nitrating Agents

A recent USSR paper deals with acetic acid-nitric acid mixtures. This paper reports data on the corrosive effect exerted by such mixtures on steel and furthermore indicates that on the basis of the experimental results described the presence in the mixtures of the unstable compound $HNO_3.CH_3COOH$ may be assumed.(6) Another paper emanating from the same research institute (the Ivanovo Chemico-Technological Institute) lists further data on the physico-chemical properties of the system acetic acid-nitric acid, describes the results of a physico-chemical investigation of the system acetic acid-nitric acid, and on the basis of the results described concludes that acetylnitrate is present in the range of equimolecular concentrations, while the anhydride of nitric acid is formed in the range of high concentrations of nitric acid.(7)

No data on the formation of tetranitromethane are contained in either of the two papers mentioned. However, the first of the two papers is immediately followed by an article which describes work that has been carried out at the Chemical Institute of Leningrad State University and deals with the physico-chemical properties of tetranitromethane-benzene mixtures.(8)

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Reduction of Nitro Compounds

Some results of an investigation dealing with the catalytic reduction of nitrobenzene have been published by members of a group active at Kazakh State University. In the work described in the published papers, the kinetics at different temperatures of the reduction of nitrobenzene, nitrosobenzene, and hydroxylamine at a skeleton nickel catalyst in alkaline and neutral media have been investigated. It was established that the rate of reduction is governed by the availability of activated hydrogen at the surface of the catalyst. Because of a shortage of activated hydrogen, the reduction proceeds in steps corresponding to the formation of intermediate products.(9) It was further demonstrated that the use of rhodium as a promoter of the nickel catalyst is effective because rhodium increases the adsorption and degree of activation of the hydrogen. The experimental data show that with nickel catalysts which contain a promoter, the reduction of nitrobenzene proceeds directly to aniline without formation of intermediate products, and that the promoter effect of rhodium is greater in an alkaline medium that a neutral medium.(10)

Research on Nitramines

A series of papers dealing with the structure, properties, and behavior of aromatic nitramines has been published by workers at the State Institute of Applied Chemistry, Leningrad.(11-14) Among the syntheses of nitramines described in the papers in question are that of E. Macciotta (nitration of potassium anilides with ethyl nitrate), that of E. Baumberger (oxidation of arylnitrosoamines with potassium ferricyanide), and that of K. Orton (nitration of arylamines with nitric acid in the presence of acetic acid and acetic anhydride). According to the published report, modifications introduced by the authors of the papers into the methods of synthesis mentioned above have resulted in improved yields of nitramines. Among the ten nitramines synthesized and used in the investigation of the structure of compounds of this class, one (p-methoxyphenyl-N-nitroamine) has not been described in the literature before. The following conclusions have been made by the authors on the basis of the experimental results obtained by them:

1. The acidity of N-nitroamines is close to that of carboxylic acids.

2. On the basis of an investigation of absorption spectra of 8 nitramines which have been melted, dissolved in carbon tetrachloride, or dissolved in benzene, it is to be assumed that the arylnitramines have the structure $ArNHNO_2$, i.e., that they are true N-nitrocompounda and do not contain tautomeric compounds of the structure ArN-NOOH.

3. The fact that the infrared absorption spectra of the sodium salts of 5 nitramines investigated in aqueous solutions exhibit the characteristic frequency of the nitro group testifies to the fact that the sodium salts have the structure of true N-nitrocompounds.

4. Under the action of aqueous solutions of alkalis, aryl-N-nitroamines retain the structure $ArNHNO_2$ and do not undergo any tautomeric transformations.

5. At low p_H values nitramines assume the structure of basic oxodiazohydrates (ArN-NOOH), while at high p_H values they retain the structure of nitraminic acids ($ArNHNO_2$).

50X1-HUM

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